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Agenda item III/1m

NEW AND IMPROVED FERTILIZER MATERIALS BASED ON UREA[1]

by

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SUMMARY

[illegible] OF UREA[1]

by

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The growth of urea production and announced plans for additional capacity indicate that urea is likely to become the world's leading nitrogen fertilizer by 1975. Therefore, consideration of new methods of utilizing urea and improving its quality is appropriate.

The usual prilled urea is too small for satisfactory use in blends and for efficient operation of broadcast spreaders. Physical strength also is comparatively low, making it subject to degradation in handling in mechanical systems. A spray drum granulation process is used by one company to produce larger granules, and a pan granulation method is also considered promising. Larger particle size also would decrease rate of moisture absorption and caking. Also, granular products have greater strength.

There is a need for improved conditioning treatments to afford better protection from moisture absorption in humid climates. Some promising organic coatings have been studied. Production of larger urea granules decreases coating weight requirements.

Wax-sulfur coatings on urea granules provide a controlled-release nitrogen fertilizer which decreases losses by leaching and volatilization, prevents burning of vegetation and damage to seedlings, and improves handling properties. Pilot-plant production of coated

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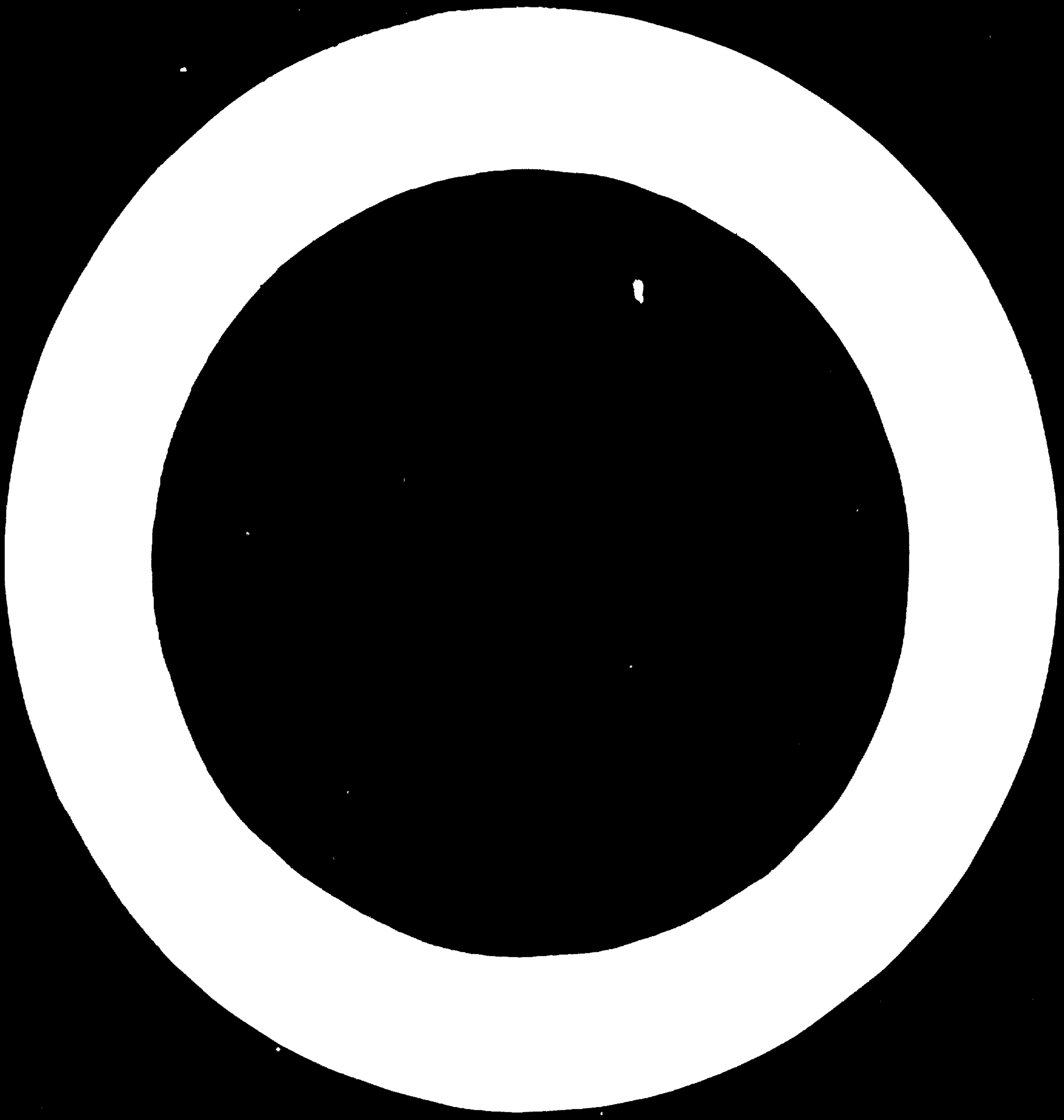

urea is described. Agronomic studies of coated urea have shown many instances of improved nitrogen utilization and increased yields. Urea-aldehyde reaction products also provide useful controlled-release fertilizers, but they are relatively expensive.

Urea-ammonium sulfate mixtures have the advantage of utilizing low-cost byproduct ammonium sulfate and supplying sulfur where that element is needed. Experiamental studies indicate that mixtures containing 34 to 40 per cent N and 3 to 4 per cent S can be prilled in oil or air or granulated in a pan granulator. The prills and granules are stronger and more resistant to abrasion than commercial prilled urea.

Use of urea in granular compound fertilizer is attractive because of its wide availability, high analysis, and freedom from fire and explosion hazards. This practice is well developed in Japan and to a lesser extent in some other countries. Because of its favorable solubility characteristics, urea is particularly useful in liquid mixed fertilizers and nitrogen solutions.

Work that is under way and additional efforts to improve properties and use of urea in compound fertilizer is keeping pace with the continuing rapid growth in urea production throughout the world.

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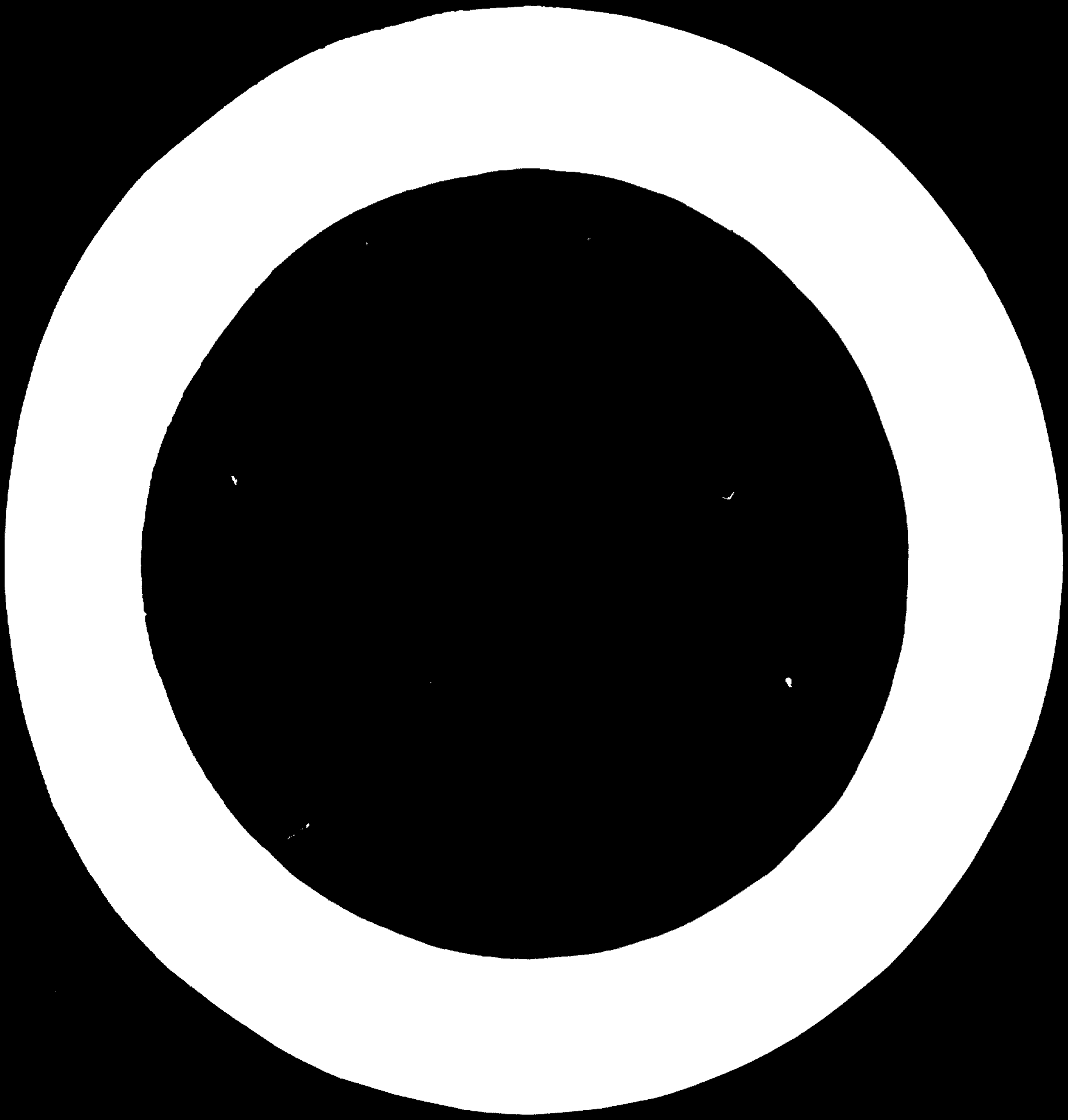

I. INTRODUCTION

1. A prominent feature of the world nitrogen industry is the rapid rise in popularity of urea, as shown in Figure 1.

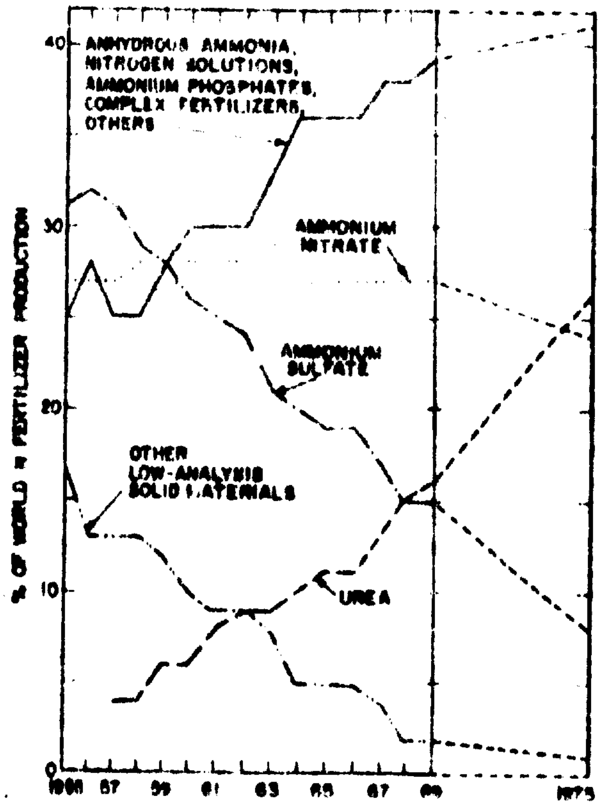

FIGURE 1
WORLD TRENDS IN TYPES OF
NITROGENOUS FERTILIZER MATERIALS

Urea's share of the world nitrogen fertilizer market has risen from less than 5% in 1955 to 16% in 1969 and is expected to increase to about 26% by 1975. These figures are based on FAO data through 1969 for the world (excepting Russia and Communist Asia) and projections based in part on estimated capacity for subsequent years. These figures are for solid urea only, and do not include the urea content of solutions. In the United States, about half of the urea used for fertilizer goes into solutions. Also, the FAO data probably do not include the urea content of some complex fertilizers.

2. The largest group consists of anhydrous ammonia, nitrogen solutions, the nitrogen content of ammonium phosphates and complex fertilizers, and miscellaneous other materials. Ammonium sulfate, once the most popular nitrogen material, supplied only 15% of the world market in 1969, and may decline to 8% in 1975. Other low-analysis materials include calcium nitrate, sodium nitrate, and calcium cyanamide. This group now supplies only 2% of the market. Ammonium nitrate now supplies 27% of the market; in future years the percentage may decline slightly.

3. The following tabulation shows estimates of world capacity for production of urea, ammonium sulfate, and ammonium nitrate in 1967, 1971, and 1975.

World nitrogen capacity,[a] 1000's of metric tons

	Ammonium sulfate[b]			Ammonium nitrate[c]			Urea		
	1967	1971	1975	1967	1971	1975	1967	1971	1975
Western Europe	1320	1570	1750	2591	3633	3,979	1426	3,071	3,320
Eastern Europe	276	300	370	1008	2402	2,500	620	1,541	2,376
Asia	916	1161	1217	300	500	500	1846	4,714	8,084
Africa	50	75	80	370	660	660	100	237	237
Oceania	30	30	30	5	85	85	15	94	94
North America	510	510	510	2015	2140	2,140	1323	2,014	2,102
Latin America	170	224	224	174	293	495	173	500	1,310
	3272	3870	4181	6463	9913	10,359	5503	12,171	17,523

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[a] Excluding Russia and Communist Asia.

[b] Includes ammonium sulfate and ammonium sulfate nitrate.

[c] Includes ammonium nitrate (33%) and ammonium nitrate - limestone (20 to 26%).

Ammonium sulfate capacity increased by about 18% from 1967 to 1971, and a further 8% increase is expected by 1975. Much of this capacity is byproduct from coking operations, caprolactam production, and other industry. Ammonium nitrate capacity increased over 50% from 1967 to 1971, but little further increase is planned. Urea capacity increased 22% from 1967 to 1971, and plans for a further increase of about 44% have been announced. These capacity estimates include materials for industrial as well as fertilizer use. They probably include urea for use in solutions and complex fertilizers in many cases.

4. It appears that, by 1975, urea will be the leading form of nitrogen fertilizer. This is particularly true in the developing countries of Asia, Africa, and Latin America where urea is expected to constitute 62% of the nitrogen fertilizer capacity.

II. IMPROVEMENTS IN PHYSICAL PROPERTIES OF UREA

5. By far the most common form of urea for fertilizer use is prilled material. Prilled urea has several disadvantages. The prills are rather small; typical samples have a high percentage in the range of 1.0 to 1.7 mm. For comparison, a common size of granular fertilizer in the United States is 1.4 to 2.8 mm. In most European countries a still larger size is preferred such as 2 to 4 mm.

6. One disadvantage of the small particle size is the relatively large surface area which increases the caking tendency and increases the rate of moisture absorption. If the prilled material is conditioned by coating, a larger amount of coating material is required.

7. When fertilizer materials are broadcast by a spinning disk spreader, the effective width of spread is decreased as the particle size decreases. Bragg (1) points out that there is a rapid fall in length of trajectory (width of spread) when the particle size decreases below 1.5 mm. This effect is likely to be accentuated with urea because of its low density. Thus, a spreader that would give satisfactory distribution with 2- to 4-mm granules would give uneven distribution with 1.0- to 1.7-mm prills at the same swath width. Even

distribution with smaller material could be obtained by decreasing the swath width, but the time required would be increased, as the machine would have to make more trips across the field. Bragg suggests that an optimum granule size for rapid, even broadcast spreading might be 3.5 to 4 mm.

8. Bulk blending is popular in the United States and some other countries. Prevention of segregation in blends requires that the particle size of the blends be closely matched. Since prilled urea is smaller than other materials commonly used in blends, it is not well suited for this use.

9. Prilled urea is fragile; its crushing strength and resistance to abrasion are much lower than most granular fertilizers. This weakness may result in excessive formation of fines in some bulk handling and conveying equipment, especially in overseas shipments. Also, some types of application equipment cause excessive disintegration.

10. In view of the disadvantages of the usual commercial prilled urea, it seems odd that so little work has been done on improving its quality. Some degree of control of particle size in the prilling process is possible, but larger droplets require a longer time to cool and solidify, and this consideration may be a limiting factor in practice.

11. One company in Canada (Cominco) is producing urea by a spray-drum granulation method. Two sizes are produced; one size, about 1.7 to 3.3 mm in diameter, is useful for bulk blending and direct application. A larger size, about 4 to 6 mm, is used for forest fertilization. The granules are harder and more resistant to abrasion than prilled material. The cost of granulation is said to be about the same as prilling.

12. TVA is developing a pan granulation process for urea in a pilot plant using an inclined pan that has a diameter of about 1 m. The usual rate of

production is about 540 kg per hour. Highly concentrated urea solutions are utilized so that drying of the product is not required.

13. A flow diagram of the process is given in Figure 2. Concentrated urea solution (98 to 99.5%) was sprayed onto a cascading bed of recycled fines in a pan granulator. The pan product was cooled in a rotary cooler by a countercurrent airflow and then screened. Undersize and crushed oversize were recycled to the granulation step.

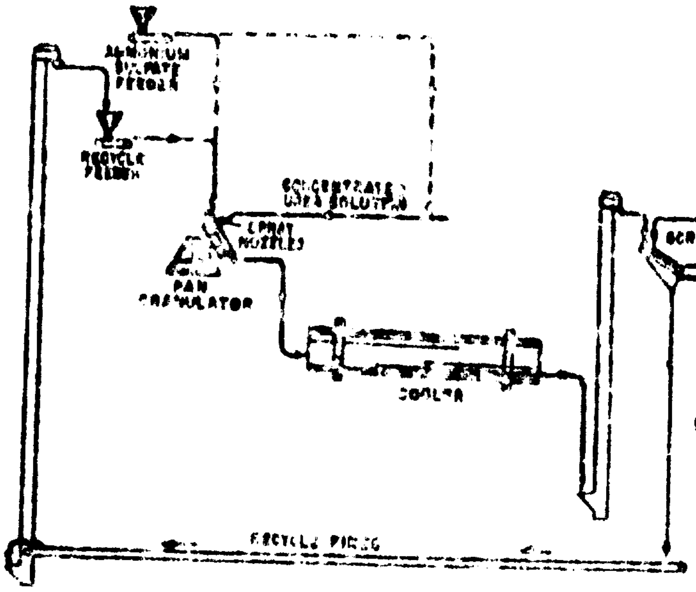

FIGURE 2
FLOW DIAGRAM OF GRANULATION PILOT PLANT FOR PRODUCTION OF UREA OR UREA-AMMONIUM SULFATE

14. Three sizes of granular urea were produced. These sizes, together with their intended end use, are shown below.

2.4 to 3.4 mm--bulk blending or direct application

2.8 to 4.0 mm--coating for controlled release

4.0 to 6.0 mm--coating and forestry fertilization

15. For granulation of all of these products, the temperature in the material in the pan granulator was carefully controlled at about 100°C. Temperature was controlled primarily by varying the recycle ratio. The normal recycle ratio was 2.5 to 3.0:1, and the temperature of the recycled material was about 56°C.

16. For the two larger sizes of urea that were to be suitable for sulfur coating, some special operating procedures were utilized to give a very well rounded and closely sized product.

a. Large, closely sized, well-rounded urea granules were used as starting recycle.

b. The product was screened in an unusually narrow size range.

c. Dust from the cyclones and crusher was not recycled to the pan. (In commercial plant operation this dust should be dissolved in the urea solution feed.)

d. The urea solution was pumped to the spray nozzles to give adequate spray pressure for good coating.

With the techniques outlined above, thin layers of urea were built up on the surfaces of the recycle. Control of granulation was so precise that only about 1% of the pan product was oversize. Product appearance was excellent. The products were particularly well rounded and smooth.

17. A tabulation of some physical properties of urea products produced in the pan granulation pilot plant is given below. Some properties of commercial air-prilled urea and Cominco granular urea are listed for comparison.

	Pan-granulated urea					Air-prilled urea	Cominco granular urea
Size of granules, mm	2.4-2.8	2.8-3.4			3.4-4.0	1.7-2.0	2.4-2.8
Solution concentration, %	99.5	99.8	99.3	98	98		
Crushing strength, kg	1.8	2.7	1.8	0.9	1.6	0.9	2.7
Degradation,[a] %	0.5	0.1	0.4	0.1	0.3	12	0.9
Apparent specific gravity	1.32	1.31	1.33	1.30	1.27	1.32	1.29
Porosity,[b] %	1.0	1.9	0.4	2.6	4.9	1.1	3.4

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[a] Percent degradation = percent minus 1.0-mm material formed on milling.

[b] Percent porosity = $100 - 100\left(\frac{\text{apparent specific gravity}}{\text{true specific gravity}}\right)$.

18. Crushing strength of the granular urea was about twice the strength of air-prilled urea. There is indication that use of the less concentrated urea solution (98%) lowered crushing strength. Also, with a given solution concentration, simply increasing the urea granule size increased the crushing strength. The resistance to abrasion of the pilot-plant granular products was greater than for commercial prilled urea. Less than 1% fines was produced in the standard test procedure as compared with 12% for the prills. The pilot-plant products had about the same crushing strength and abrasion resistance as commercial granular urea (Cominco).

19. Results to date do not show any significant difference in the bulk density and specific gravity of the pan products as compared with air-prilled urea. The calculated porosity of the granules indicated that the pan-granulated urea made with 99+% solution had about 1% voids which is similar to prilled urea and less porous than Cominco urea. The pan-granulated urea made with 98% solution was more porous (3 to 5% porosity).

20. The pan granulation process is being used successfully in a full-scale plant (20 tons/h) by TVA to granulate high-nitrogen fertilizers containing ammonium nitrate including ammonium nitrate sulfate (30-0-0-5S) and ammonium phosphate nitrate (30-10-0) (2).

III. COATING AND CONDITIONING UREA

21. Although some urea is marketed without conditioner, most of it now is conditioned either with a very finely divided inert dust such as kaolin clay or with one of several organic materials. These treatments generally are effective in preventing caking while stored in moistureproof bags, but none of these treatments is effective in retarding the rate of moisture absorption

when the material is in contact with humid air above the critical relative humidity which is about 75% at 30°C.

Coating Urea To Retard Moisture Absorption

22. In some parts of the United States where the climate is hot and humid, there is a need for a conditioning treatment that will significantly retard moisture absorption. The need is even greater in some tropical areas where production and use are likely to be large. A petrolatum-rosin-paraffin (PRP) coating was developed 25 years ago and was used on grained ammonium nitrate (3). It was moderately effective in retarding moisture absorption, but its use was discontinued when it was realized that it contributed to explosion hazard.

23. Recently, test quantities of granular urea (1.7 to 3.3 mm) were coated with 2.5% PRP. Effectiveness of the coating was judged by exposing samples of coated and uncoated urea to turbulent air at 32°C and 90% relative humidity for 24 hours. The coated urea became slightly damp but remained free flowing; the uncoated urea became slushy; the particles lost their identity. The rate of moisture absorption for the coated material was only about one-fifth that of the uncoated. Numerous other coating materials are being tested in an effort to identify low-cost effective treatments.

24. The Dutch State Mines is reported to have developed an effective oil coating treatment. In all coating treatments, larger size granules are helpful because the smaller surface area per unit weight reduces the required quantity of coating material.

Coating Urea for Controlled Release of Nitrogen

25. A nitrogen fertilizer with controlled release has been the objective of considerable research. Potential advantages of controlled-release nitrogen fertilizers are increased efficiency of uptake by plants; minimization of losses by leaching, runoff, or decomposition; reduction of application costs through reduction in frequency of application; elimination of luxury consumption; prevention of pollution of ground water, streams, and lakes; and prevention of burning of vegetation or damage to seedlings.

26. In general, the research has been divided into two broad categories; one approach has been the synthesis of nitrogen compounds with desired solubility characteristics, and the other has been the coating of soluble fertilizers. Examples of synthesized compounds that dissolve slowly are urea-formaldehyde products, isobutylidene diurea, and crotonylidene diurea, but the relatively high cost of these products limits consumption to specialty uses. In a search for more promising materials, about 100 nitrogen-containing materials were evaluated by TVA in greenhouse tests. Some were inert, some were toxic, some were readily available to plants, and some were slowly available. From the latter group, oxamide (32% N) was selected as the most promising, and several years' study was made of potential manufacturing processes. However, it was concluded that the manufacturing cost would be too high for farm fertilizer use.

27. Attention was then turned to coating nitrogen fertilizers to control release. Of the several coating materials that were tried or considered, sulfur was selected on the basis of cost and effectiveness. Of materials to be coated, urea was selected on the basis of cost, availability, and high

concentration. Research at TVA on sulfur coating of urea particles for controlling the dissolution rate began in 1961.

28. However, sulfur alone was not very resistant to moisture penetration, and it was the discovery that an oily sealant was required with the sulfur that provided the breakthrough to a successful coating. It is believed that the oil acts as a sealant in filling the fine pores in the sulfur shell. Ordinary motor oil worked very well with water dissolution measurements in the laboratory; however, in soil, the coating failed because the soil mechanically removed the oil by absorption. Petrolatum worked better in the soil, but certain types of wax were found to work even better and were cheaper than petrolatum. These waxes contain about 10% oil; waxes containing only 1 or 2% oil are unsatisfactory as sealants, even in water. Therefore, it was deduced that the oil provides the sealing action, and the wax provides mechanical protection that prevents the oil from being absorbed by the soil.

29. It was found that the wax was subject to microbial attack in the soil which destroyed its sealing properties; therefore, it was desirable to add a microbicide. Coal tar has been found to be an effective, cheap microbicide. Only about 0.2% coal tar is required.

30. Early development work was carried out in the laboratory by coating batches of urea in 15- and 56-cm-diameter drums (4). Later the development was continued in a small continuous pilot plant; the production rate was about 135 kg per hour (5). At present the process is being developed further in a large pilot plant that has a capacity of about 1 ton per hour. The initial operation of the large pilot plant has been quite encouraging.

31. A schematic flow diagram of the pilot plant is shown in Figure 3. Granular urea is preheated in the first rotating drum to 80°C with electric

radiant heaters to prevent the sulfur from freezing too rapidly on the granules. The molten sulfur is air-atomized and sprayed onto the rolling bed of granules in the second drum. Wax and coal tar are applied in the third drum. The coated granules are then cooled in a fluidized bed cooler, and a powdery conditioner is applied in a fourth drum to eliminate the tacky condition of the wax.

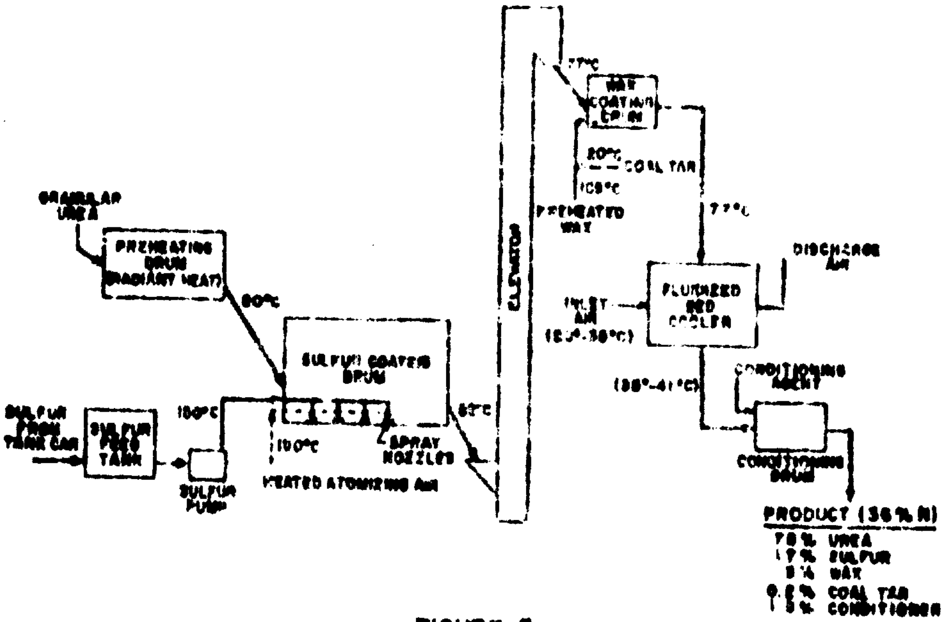

FIGURE 3
FLOW DIAGRAM FOR SULFUR-COATED UREA PILOT PLANT

32. Most of the work was done with commercial granular urea (1.7 to 3.3 mm) produced by the previously mentioned spray-drum granulation process. Some tests were made with prilled urea, but its smaller particle size results in greater surface area per unit weight of urea; this greater surface requires a coating that is higher in percentage by weight of the product for a given coating thickness. For this reason large, well-rounded granules are preferred for coating.

33. One cause of the long period required for development of the coating is the time required inherently for agronomic testing of the experimental products. Another cause is the large number of operating variables that

affect the quality of the coating. Fourteen variables, some interacting, affecting coating quality have been identified. However, in spite of the large number of variables, they all can be controlled fairly easily to give a consistently uniform product. The difficulty is in finding the optimum combination of variables.

34. In the small pilot plant the best quality of coating produced at a coating weight of 16% had a dissolution rate of 18% in the first 7 days and 0.6% per day for the next 7 days. These dissolution rates were determined in the laboratory by immersion in water at 38°C. The higher initial rate of dissolution results from the presence of some granules that are coated imperfectly when they pass under the three spray nozzles in the drum. These granules dissolve in a short time when a sample is placed in water. The remaining granules that are well coated have an average daily dissolution rate that is relatively constant. For most purposes it is desirable to have a portion of the nitrogen readily available immediately after application of the fertilizer. By varying the coating thickness (or weight), both the initial rate and daily rate of release can be controlled. The desired rate for a given crop and climate has to be determined by field testing.

35. The effect of time, coating weight, and temperature on dissolution in water is shown in Figure 4. These results were obtained with materials produced in the small pilot plant before optimum coating procedures were developed; in subsequent work, similar results were obtained with lighter coatings. Dissolution rates in the soil are not necessarily the same as in water, as many other variables affect soil dissolution rates.

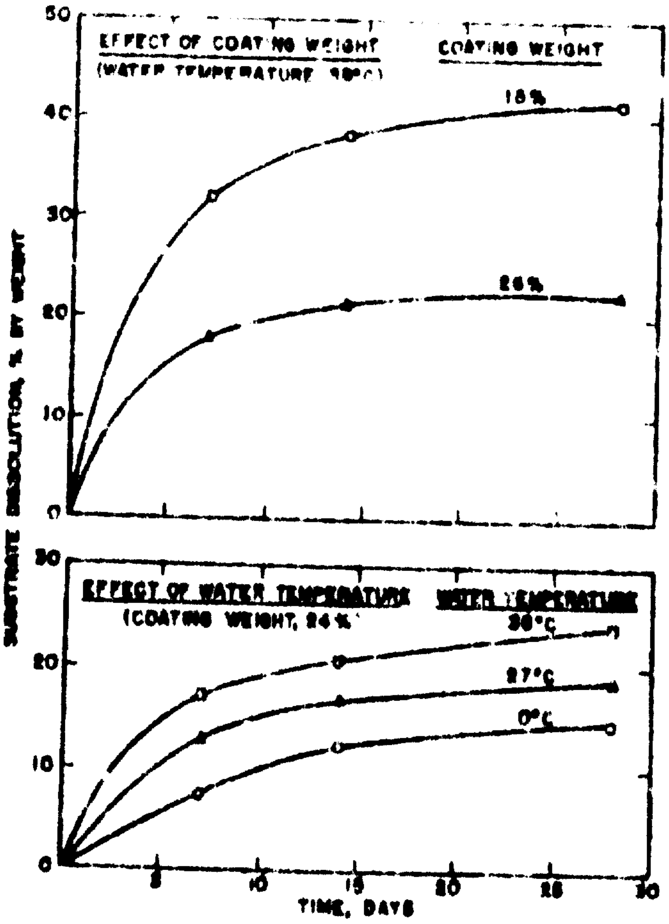

FIGURE 4
SUBSTRATE DISSOLUTION IN WATER VERSUS TIME OF IMMERSION OF SULFUR-COATED SPRAY-DRUM-GRANULATED UREAS (1.7 TO 3.4 mm)

36. Estimates indicate that the cost of coating granular urea in a plant of 450 metric tons per day capacity would be about $16 per ton, including a 15% return on investment. If the price of straight urea (46% N) is $77 per ton, the estimated price of coated urea (36% N) would be $76 per ton, which is about 26% more per unit of nitrogen. It is recognized that initial production on a smaller scale will be more expensive. Also, transportation costs per unit of nitrogen will be greater for the coated material because of its lower nitrogen content. However, the results of agronomic tests indicate that there are many cases in which the value of increased yield would more than pay for the higher cost. Moreover, a major advantage of coated urea is the potential

reduction in costs by applying the nitrogen only once at the time of planting rather than having the added costs of top- or side-dressing.

37. In addition to the controlled-release characteristics, coated urea has excellent storage and handling characteristics and might even be handled in bulk in humid climates.

Agronomic Tests of Coated Urea

38. The agronomic response of various crops to sulfur-coated urea has been reported by TVA agronomists in several publications (6, 7, 8). Results or conclusions obtained are summarized below.

a. A single application of sulfur-coated urea on coastal bermuda grass in the spring gave as good or better results than four (split) applications of ammonium nitrate.

b. Excessive (luxury) consumption and excessive growth of grass forage shortly after a single application were avoided with sulfur-coated urea.

c. Sulfur-coated urea produced better distribution of protein throughout the forage growth period.

d. The sulfur residues oxidize slowly to plant-available sulfate.

e. Heavy surface application of sulfur-coated urea to grasses did not result in burning or N (decomposition) losses as with uncoated urea.

f. Sulfur-coated urea resisted leaching and denitrification in cases of heavy rainfall and resulted in higher yields under these conditions.

39. Tests of sulfur-coated urea are being carried out in 36 of the United States and in 22 foreign countries. Some of the results of these tests indicated that coated urea was advantageous for use on sugarcane, pineapple, rice grown with delayed or intermittent flooding, and in general for long-season

crops and for conditions where high leaching or decomposition losses are prevalent.

40. The sulfur-coating technique may be applied to fertilizers other than urea. Experimental work has included coating of diammonium phosphate, potassium chloride, potassium sulfate, and various compound fertilizers.

IV. UREA - AMMONIUM SULFATE

41. Combinations of urea and ammonium sulfate (UAS) are of interest because byproduct ammonium sulfate is available at low cost at many locations, and because sulfur is an essential element for plant growth. Recent reports by The Sulphur Institute show that moderate to serious sulfur deficiencies occur in more than half of the United States and in at least 47 other countries, including several developing countries.

42. Experiments by TVA have shown the feasibility of prilling UAS in oil (9). Mixtures containing 18 to 60% ammonium sulfate have been prilled successfully in the pilot plant. The corresponding nitrogen contents are 40 to 30%, and the equivalent elemental sulfur contents are 4 to 13%.

43. The usual temperature of the UAS mixture for prilling was about 135°C. Figure 5 shows a phase diagram of the UAS system. The system shows a eutectic at 9% ammonium sulfate and 91% urea with a melting point of 121.5°C. Mixtures containing more than about 10% ammonium sulfate at the usual prilling temperature of 135°C contained undissolved solid ammonium sulfate suspended in the melt. However, these mixtures were fluid enough for successful prilling using a rotating prilling cup 7.5 cm in diameter containing 24 holes of 2-mm diameter. The prills were somewhat larger and stronger than air-prilled urea.

Also, tests indicated that prilling in air would be feasible with minor changes in conventional urea plants.

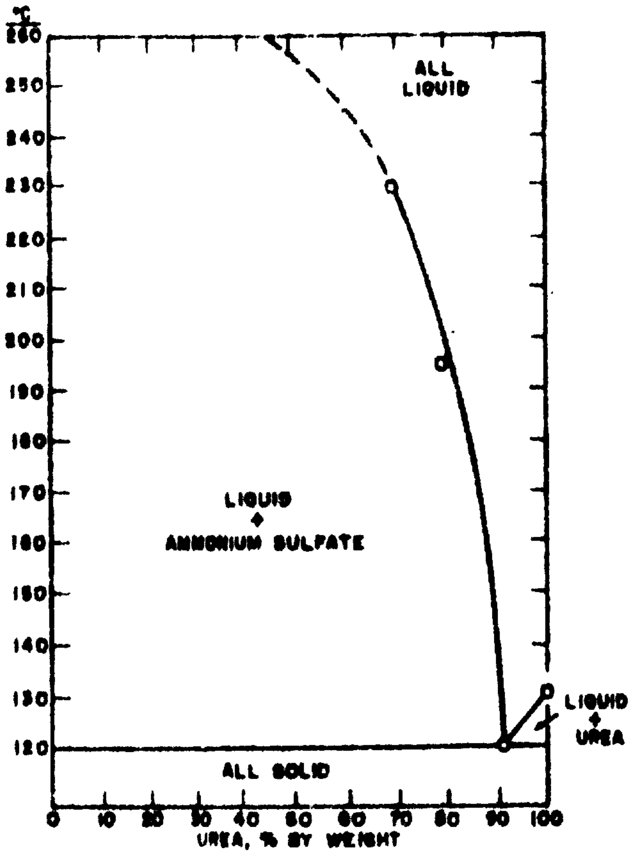

FIGURE 5
PHASE DIAGRAM OF SYSTEM UREA-AMMONIUM SULFATE

44. Granular UAS has been produced successfully in the pan granulation pilot plant that was mentioned earlier. Figure 2 shows optional addition of ammonium sulfate in the urea granulation process.

45. The ammonium sulfate used was a crystalline material, a byproduct from the steel industry, mainly smaller than 0.5 mm. Urea solution was prepared by melting prilled urea with about 1% water in a steam-heated melter. In some tests, ammonium sulfate was added to the urea in the melter. As much as 20% ammonium sulfate (not necessarily a maximum) could be added to the urea without encountering difficulty in spraying the melt into the pan granulator. This method gave generally better results than addition of ammonium sulfate

in a dry state with the recycle. A mixture of 20% ammonium sulfate and 80% urea provides a product grade of 40% N and about 4.5% S (after conditioning). This grade is deemed useful for use in sulfur-deficient areas.

46. The finished granules (2.4 to 3.4 mm) appeared to have good physical properties, although storage tests have not been completed. Since UAS has a lower critical relative humidity than either urea or ammonium sulfate, it is expected that conditioning will be required.

47. In work reported by Joris and Sor (10), it was found that UAS may be granulated by air prilling, roll compaction, or drum granulation. These products contained 33 to 34% N (approximately equal weights of urea and ammonium sulfate). The products were stronger than urea prills.

48. Joris and Sor (10) report that volatilization loss (as NH_3) from UAS applied on the surface of the soil was much less than from straight urea. Also, agronomic tests in several locations gave better results than ammonium nitrate, presumably due to the sulfur content of UAS.

V. USE OF UREA IN COMPOUND FERTILIZERS

49. Compound fertilizers are growing in popularity in many countries. In Western Europe during the period of 1958 to 1969, compound fertilizers increased from about 35 to 58% of all fertilizers. In Japan in 1969, 72% of the N, 76% of the P_2O_5, and 84% of the K_2O were in the form of compound fertilizers.

50. There is also an increasing preference for compound fertilizers in many developing countries. When a country begins to use fertilizer, nitrogen is often the limiting factor, but after a few years of use of straight nitrogen,

the native supply of other elements in the soil often becomes depleted and must be supplied.

51. While it is possible to apply straight fertilizers separately, it usually is more convenient and satisfactory to use a compound fertilizer containing all necessary elements.

52. Urea is well adapted to use in compound fertilizers because of its high analysis, low cost per unit of nitrogen, and plentiful supply. In comparison with ammonium nitrate, it is free from fire and explosion hazards, and agronomically preferable for rice.

53. Compound fertilizers formulated with urea and superphosphate have some advantages that should not be overlooked. Superphosphate production is a simple process, and often may be the best means for utilizing byproduct sulfuric acid when the quantity is insufficient for an economical scale of phosphoric acid production. Also, superphosphate supplies sulfur, an element necessary for plant growth and often deficient. Many developing countries have superphosphate facilities that are not fully utilized. Granulation of superphosphate with urea and other materials offers a means for providing good-quality compound fertilizers that are adapted to the needs of crops and soils in local areas.

54. The technology of utilizing urea in granular compound fertilizers is well advanced in Great Britain where several small plants supply local needs using formulations containing urea, superphosphate, potash salts, and often ammonium sulfate. Quite often, ammonium phosphate is added to up-grade the product. Some popular grades are 10-10-16, 20-10-10, and 14-14-14. A recent article summarized British practice (11).

55. In visiting some of the British plants, the near absence of fume and dust was a noteworthy feature even though no sophisticated pollution control equipment was used. Subsequently, TVA pilot-plant tests have confirmed that granulation of urea-superphosphate formulations yields much less fume and dust than the ammonium nitrate-containing formulations commonly used in the United States.

56. Use of urea in granular compound fertilizers is also common in Japan where a wide range of grades is produced and many types of granulators are used. Ando (12) has presented an excellent survey of granulation practice in Japan.

57. In the United States, urea is used widely in liquid mixed fertilizers and to some extent in bulk blends, but so far it has not been used to an appreciable extent in granular compound fertilizers.

58. An interesting possibility is the production of urea phosphate and its use as an intermediate in making liquid and solid fertilizers, as described in a recent paper by Nayar and Gopinath (13). Essentially pure urea phosphate, $CO(NH_2)_2 \cdot H_3PO_4$, was produced by reaction of urea with filter-grade, wet-process acid and separated by evaporation, cooling, crystallization, and centrifuging. The product may be used directly as a fertilizer or converted to ammonium orthophosphate or polyphosphate by heating with or without excess urea. In one example a 15-35-0 liquid fertilizer was produced from the pyrolyzed melt. Subsequent laboratory-scale studies by TVA have confirmed the technical feasibility of the process, and further development is likely.

VI. UREA - AMMONIUM PHOSPHATES

59. Compound fertilizers containing urea and ammonium phosphate are of particular interest because they are the highest analysis N-P (and N-P-K) compound fertilizers that can be produced by present technology. The actual grade depends on the purity of the ammonium phosphate and on whether the ammonium phosphate is monoammonium or diammonium phosphate or ammonium polyphosphate or some mixture of these compounds. The grade also depends on the amount of conditioner and other materials that may be added.

60. Combinations of pure urea and pure diammonium phosphate or ammonium polyphosphate will yield grades as high as 30-30-0 or (with KCl) 20-20-20. When using ammonium phosphate prepared from typical wet-process acid, 28-28-0 and 18-18-18 are easily attained, even when allowance is made for conditioner.

61. At present, urea - ammonium phosphate (UAP) is known to be commercially produced in India (<u>14</u>) and Japan (<u>12</u>). As pointed out previously, many plants use formulations containing urea and ammonium phosphates along with other lower analysis materials.

62. Processes for producing UAP may be classified according to whether the ammonium phosphate is supplied to the granulator as a slurry, a solid, or a melt. Likewise, the urea may be supplied as a solid or as a highly concentrated solution approaching a melt. Obviously, if the ammonium phosphate and urea are produced at the same site, UAP could be produced by any of these combinations. If the two materials are produced at separate locations, it usually is necessary to transport either the urea or the ammonium phosphate or both to the granulation plant in solid form. (As an exception, certain grades

of UAP such as 15-30-15 can be made from urea-ammonia solution and phosphoric acid.)

63. In a plant in India where both urea and ammonium phosphate are available, a 28-28-0 product is made by supplying ammonium phosphate as a slurry and urea as a solid (prills). The ammonium phosphate slurry and prilled urea are fed to an ammoniator-granulator where granules are formed by coating the prills with the slurry (<u>15</u>). Ammonia is supplied also to the granulator to convert the ammonium phosphate slurry to diammonium phosphate.

64. In Japan (<u>12</u>), various combinations of solid and slurry ammonium phosphate with solid and solution urea are used to make high-analysis granular fertilizers. Types of granulators used include rotary drums, pans, pug mills, and others.

65. Slack (<u>16</u>) has reviewed the technology of producing granular complex fertilizers including UAP.

66. Fisons (<u>11</u>) has developed a process in which UAP is produced from solid nongranular monoammonium phosphate and prilled or crystalline urea. The mixture of two materials is granulated with the aid of steam in a rotary drum or pug mill. Other materials may be added if desired. Some of the grades mentioned are 24-30-0, 28-28-0, and 19-19-19. The process has the advantage that it can be carried out in small granulation plants using shipped-in materials.

67. TVA has studied production of UAP extensively on a pilot-plant scale. Since TVA's plans provided for coexisting urea, ammonia, and phosphoric acid facilities, the main emphasis was placed on direct production from these materials in order to avoid the expense of separate production of solid intermediates (urea or ammonium phosphate).

68. The first process that was developed was essentially the well-known TVA diammonium phosphate process (17) except that urea solution was added in the ammoniator. The results of this work have been published (18).

69. Some problems were encountered in drying UAP products. It was desirable to dry the products to a low moisture content (about 1%) to ensure good storage properties. The temperature of the material leaving the dryer was limited to about 95°C to avoid decomposition of the urea by hydrolysis. It was found necessary to limit the temperature of the air entering the rotary dryer to a range of 150° to 175°C for countercurrent flow, or about 200°C for cocurrent flow, to prevent the material from melting and sticking to the shell and flights of the dryer. Because of these limitations, the drying rate was slow, and a long retention time would be required to reduce the moisture content below 1%. As a result the dryer would have to be very large and expensive.

70. Attention was then turned to melt-granulation processes in which no drying is necessary. Ammonium phosphate melts may be produced by a process developed by TVA in which the heat of reaction of ammonia and phosphoric acid is utilized to evaporate the water in the acid and convert part of the phosphate to polyphosphate. Anhydrous ammonium phosphate melts should contain some minimum proportion of polyphosphate to be fluid enough to handle easily. The minimum polyphosphate content for satisfactory fluidity is not well defined; 20% is adequate, but not necessarily a minimum.

71. Urea melt may be obtained by concentrating urea solution to less than 1% water. Use of this melt with anhydrous ammonium phosphate melt provides an essentially water-free system, eliminating the need for drying.

72. Oil prilling of the mixed melt was studied in a pilot plant. The ammonium polyphosphate melt at about 200°C was mixed with urea melt at about 150°C and

a small amount of cool recycle. The resulting mixture at a temperature of 135°C could be prilled satisfactorily in a rotating prilling cup (19). The prills were collected in a vessel containing cooled oil and separated from the oil by centrifuging. One reason for selecting prilling in oil rather than in air was that materials of high polyphosphate content crystallized too slowly for air prilling. Probably air prilling would have been satisfactory for low-polyphosphate materials, but high-polyphosphate products were desired for possible use in liquid fertilizers. Oil-prilled products from this pilot plant (using electric-furnace phosphoric acid) included 30-30-0, 36-18-0, and 39-13-0.

73. In attempting to scale up the process to a 400-ton-per-day unit, several difficulties became apparent. These difficulties need not be enumerated. However, there was one major drawback to prilling UAP melts in either oil or air; when the ammonium phosphate melt was made with wet-process acid, it reacted rapidly with the urea melt, forming a foamy mixture that was very difficult to prill.

74. Attention was then turned to cogranulation of urea and ammonium polyphosphate melts in a pug mill. In this process the two melts are added at separate points in the pug mill. The temperature in the pug mill is controlled at about 85°C by recycling cooled product. This process has proved satisfactory in a pilot plant of 0.5 ton per day capacity. The results have been described (20).

75. The UAP products made by the pug mill process showed unexpectedly good physical properties, especially when made with wet-process acid. Although the critical relative humidity is comparable with that of ammonium nitrate, the rate of moisture absorption was less, and the rate of penetration of moisture

into the material in open piles was slow. Also, the material did not become wet after absorbing a limited amount of moisture. This behavior has not been fully explained, but it probably is connected with the presence of polyphosphate.

76. The main disadvantage of the pug mill process is that the high levels of polyphosphate content cause difficulty in granulation because of slow crystallization and plasticity, especially when the phosphate is derived from wet-process acid. For instance, in producing a 28-28-0 UAP, the granulation step becomes difficult when more than 25% of the P_2O_5 is present as polyphosphate. This is a disadvantage only when the product is expected to be useful in making liquid fertilizer.

77. Materials containing polyphosphate have a high P_2O_5 water solubility, usually 98 to 100%, whereas ammonium orthophosphates made from some types of wet-process acid may have 90% or less of the P_2O_5 in a water-soluble form. The higher water solubility is a practical advantage in countries where water solubility is the accepted standard for determining the commercial value of phosphate fertilizer.

78. Design of a 400-ton-per-day demonstration-scale plant to produce UAP has been started. In the meantime, further pilot-plant work is under way. It is planned to use wet-process phosphoric acid (50 to 54% P_2O_5) and to produce low-polyphosphate melts by the direct process (21). The phosphate melt will be combined with urea melt in the pug mill. The grades planned for production are 36-18-0, 28-28-0, and 21-42-0. Potash-containing grades have been made in the pilot plant, but none will be made in the larger scale plant. It is expected that the main uses of the product will be for direct application in areas where potash is not needed, and for use in bulk blending where potash will be added.

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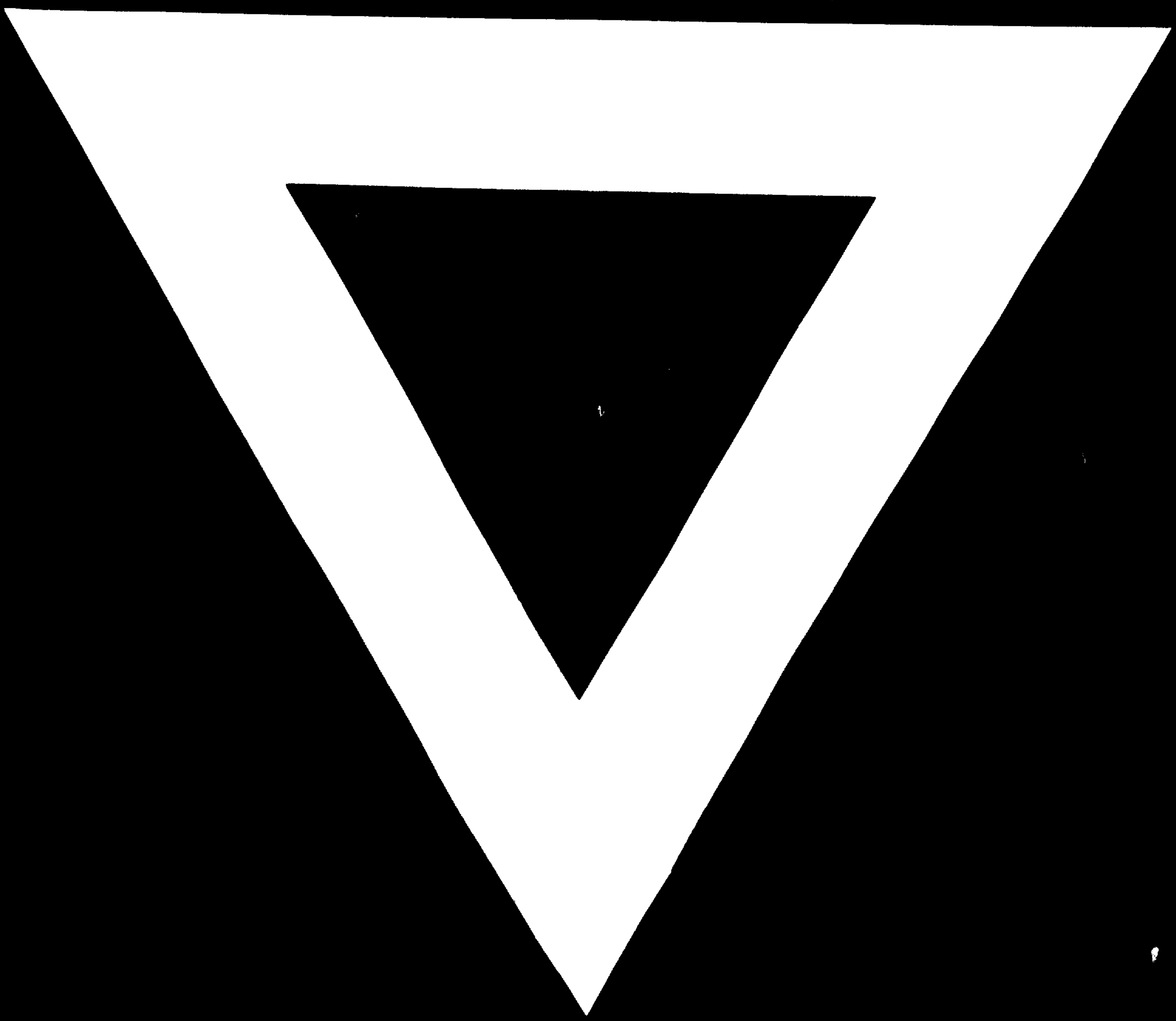

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